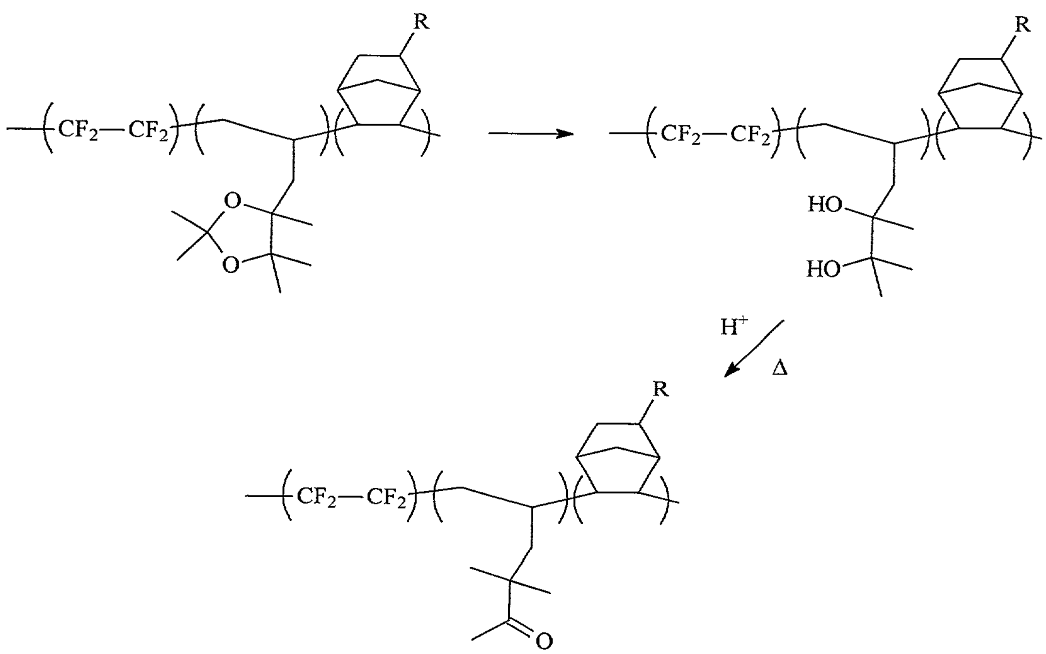
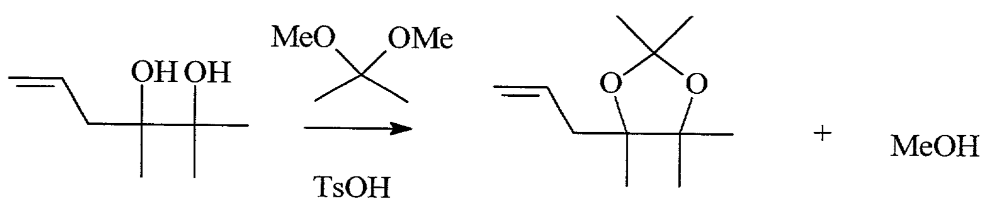
The invention encompasses negative-tone and positive-tone resists including, without limitation, those described herein.

Negative-tone resists are ones going from less polar to more polar by a wide range of chemistries known to those familiar in the art. The polarity change is typically brought about by an acid catalyzed reaction that causes a change in functional group. Negative-tone resists from a change in molecular weight, including crosslinking etc.

Positive-tone resists are ones going from a more polar group going to a less-polar group. Examples include, but not limited to, those set forth above and the pinacol rearrangement:



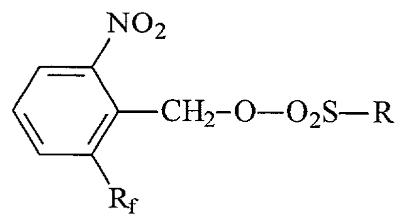
Synthesis of pinacol monomer:



A number of photoacid generators can be used including, without limitation, those known to one skilled in the art. Examples of PAGs include triaryl sulfonium salts and diaryliodonium salts with perfluoroalkyl sulfonates

as the anion. Other anions included are those found in U.S. Patent No. 5,554,664, the disclosure of which is incorporated herein by reference in its entirety such as, without limitation, perfluoroalkyl sulfonyl imides and perfluoroalkyl sulfonyl methides. These PAGs are believed to have enhanced solubility characteristics and acidity.

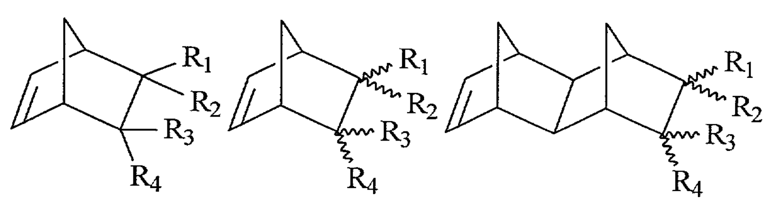
Another example of a PAG which may be employed:



Preferably, R_f is a fluoroalkyl substituent. It is preferred that the number of carbon atoms in the fluoroalkyl group range from 4 to 12, although other values are encompassed by the invention. Although not intending to be bound by any theory, it is believed that this range is optimal for controlled solubility and glass transition temperature (T_g). Most preferably, the number of carbons is 6.

Preferably, R is either a fluoroalkyl substituent or an aryl-containing group (e.g., benzene or p-toluene). It is believed that the more acidic the sulfonic acid, the less stable the compound.

Examples of monomers and polymers that may be used include:



R_1	R_2	R_3	R_4
F	F	F	F
F	F	F	R_f
H	H	H	R_f
R_f	H	H	R_f
H	H	CH_3	$COOR_f$
H	H	H	$COOR_f$
			$(CH_2)_nR_f$ n=1,2
R_f	F	F	R_f

wherein R_1, R_2, R_3, and R_4 are defined in the table above. The above monomers may be used for copolymerization with other monomers disclosed herein. Preferred monomers for use in copolymerization include, without limitation, tetrafluoroethylene and hexafluoropropylene.

This invention addresses problems associated with image collapse, resist transparency at 157 nm, potential solubility problems of new resist materials in a readily available solvent, elimination of organic solvents and aqueous developers (i.e., turning a wet process into a dry process). The invention uses differences in polarity to create solubility differences in supercritical and liquid CO_2.

The present invention may be used for the manufacture of semiconductor devices. In addition, the invention may be used for other non-lithographic processes in which a polymer must be deposited and removed from a surface in a controlled fashion (e.g., coating of low-k dielectrics, coating on solid substrates, fiber optics, optical components, glass, ceramics, metal, and plastics).

In the event that photoresist etch resistance difficulties may exist, such problems can be addressed by structure modification to make the polymers more resistant to etch. In the event that the polymers display adhesion problems, the CO_2 deposition process can help to potentially mitigate the difficulty in wetting the surface and reduce the chance of potentially catastrophic defects.

The invention has been described with respect to the preferred embodiments set forth above. It should be appreciated that these